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METHOD OF TREATING BLACK GREASE AND PRODUCT THEREOF

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21 Claims. (Cl. 260—409)

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The present invention is directed to the treatment of black grease or acidulated soap stock to produce more valuable products therefrom.

More particularly, the invention is directed to a method of treating black grease to produce a new and more valuable esterified black grease product, and a new esterified and hydrogenated product, therefrom. The invention includes a new method of treating black grease to effect esterification thereof; a new esterified black grease product; a new method of esterifying and hydrogenating black grease; and the new esterified and hydrogenated product. The present application is a continuation-in-part of my now abandoned copending application Serial No. 730,199, entitled "Hydrogenation of Oils and Product Thereof."

The black grease or acidulated soap stock used as starting material in the present invention is the product obtained by the alkali refining of glyceride oils and fats with subsequent acidulation of the soap stock resulting therefrom.

The soap stock formed in the caustic alkali refining of such oils and fats consists largely of the alkali metal salts of the free fatty acids and contains free oil entrained by the other constituents. It also carries coloring matters and other substances originally existing in the crude oil including phosphatides, sterols and glucosides. The soap stock contains, for example, about 15% of free oil, 35% of fatty acids in the form of soap, 8% or more of phosphatides and unsaponifiables, and small amounts of coloring matters, etc., the balance being water. In batch refined soya bean oil, the soap stock may contain 20–25% of phosphatides on a dry basis, and in continuous refined soya soap stock there may be as much as 33% of said phosphatides.

This soap stock is a low grade by-product or waste material and has had very little use in the past. It has been treated to some extent with strong caustic alkali to convert the oils into soap; but the soap so produced has been of inferior grade and sold very cheaply on the market.

In order to recover the fatty material from the soap stock it has also been treated by means of a mineral acid, such as a solution of sulphuric acid, to acidulate the same and to free the fatty acids from combination with alkali, together with the free oil. In this treatment, some of the other constituents like phosphatides are split by the acid treatment, and, according to Jamieson in the book entitled "Vegetable Fats and Oils" (1943), page 369, the phosphatides might

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be expected to decompose into glyceryl phosphoric acid, choline, free fatty acids and even free phosphoric acid. The oily constituents are removed from the water and the resulting dark colored product is known as acidulated soap stock or black grease. A typical black grease contains from 35% to 95% of total fat including usually 40% to 70% of free fatty acids, together with about 6% of miscellaneous substances including sterols and other residues of acidulation, and also a tarry residue of a very dark color from which the name "black grease" is derived. The amount of free fatty acids in black grease may vary considerably and may be from 25% to 75%. A small but substantial amount of free water is usually present in the black grease.

The black grease has not been capable of any industrial use in its original state. It has been customary to further acid treat the same to split the oil content into free fatty acids and subject the same to steam distillation under high vacuum to distill off the fatty acids. In this operation there has been a considerable loss, in the neighborhood of, e. g., 20%, of the fatty acids contained in the black grease, with the formation of a by-product known as pitch or tar, which usually is of practically no value and interferes with the production of pure fatty acids. The distilled fatty acids have been of inferior quality and even though they are redistilled under vacuum they are sufficiently impure so that their use has been restricted. The distillation process is complicated and expensive and requires considerable control in order to obtain a satisfactory distilled product.

The present invention provides an improved process for treating black grease, by a relatively simple and inexpensive procedure, whereby substantially the entire fatty acid and oil content of the black grease can be recovered in the form of a new and valuable product.

While the hydrogenation of refined oils and fats, freed from the major portion of their impurities by the alkali refining treatment, is a common practice in the art, black grease has not heretofore, so far as I am aware, been hydrogenated or considered capable of being successfully hydrogenated. The refining of the oils results in a concentration of the impurities in the soap stock and in the black grease produced therefrom, so that the black grease differs radically in its composition from that of the refined oils commonly hydrogenated. It is well known that the presence of various impurities in unrefined crude oils interferes with their hydrogena-

tion; and the large concentration of impurities in the black grease might well be considered to interfere with or prevent successful hydrogenation thereof.

In attempting to hydrogenate black grease by the usual hydrogenation procedure I have encountered unexpected difficulties, due not so much to the impurities which might be considered to be catalyst poisons, but, as I discovered, to the water contained in the black grease and formed by chemical reaction therein during the attempted hydrogenation, and which is so large as to present a difficult foaming problem, if an attempt is made to remove the water vapor, while if not removed, it interferes with or prevents the hydrogenation reaction.

I have further discovered that by gradually heating the black grease to an elevated temperature under regulated conditions prior to hydrogenation a profound change takes place in the composition of the black grease due to esterification reactions taking place between the black grease constituents; and that the resulting esterified black grease, in contrast with the black grease before such treatment, can be readily hydrogenated by subjecting it to usual methods of hydrogenation.

Black grease is difficult to analyze to determine its constituents. Its fatty constituents are commonly considered to be made up of free fatty acids and neutral oil or triglycerides. The difficulty in determining the nature and amount of other constituents doubtless explains the limited knowledge of the art regarding them. Thus, it is not known or recognized, so far as I am aware, that diglycerides or other esterifiable constituents are present to any substantial extent in the black grease. I have found, however, that such esterifiable constituents, including diglycerides, are present to a surprising extent in the black grease and that the subjecting of the black grease to regulated heating to effect esterification of such constituents with part of the fatty acid of the black grease results in a surprising reduction in the free fatty acid content of the black grease ranging, for example, from around 6.7% to around 15.2% and with an average of around 10.9% in a number of runs in which the reduction in free fatty acid content was determined. This reduction in free fatty acid content of the black grease on esterification is accompanied by a corresponding increase in fatty acid esters formed by reaction of the fatty acids with the esterifiable constituents of the black grease, with accompanying evolution of water of reaction.

Analytical methods make it difficult to determine the nature and amounts of the different esterifiable constituents contained in the black grease, but I am led to believe that they consist largely of diglycerides, or of diglycerides and monoglycerides, which are in part set free from phosphatides by the acidulation treatment and in part extracted from the crude oil during the refining treatment. Alcohols such as sterols, contained only to the extent of a small fraction of a percent in the crude oils, are concentrated in the soap stock and black grease, including free sterols set free from glucoside impurities; and even though only a few percent of such sterols or esterifiable alcohols may be present in the black grease they apparently undergo esterification to a greater or less extent at the same time that diglycerides are esterified, and are present in the esterified black grease to a greater or less extent as sterol or other alcohol esters.

The profound change in the composition of the black grease due to the esterification treatment results in a product of lower viscosity or increased fluidity than the black grease treated, and which does not emulsify or foam, due apparently to the conversion of diglycerides and other esterifiable and emulsifying constituents into esters of lower melting point.

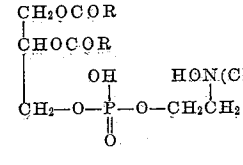
I have found that not only does the esterification and drying of the black grease convert it into a product which can be readily hydrogenated; but I have found that the esterification and subsequent hydrogenation can advantageously be combined as successive operations in the hydrogenation apparatus, by subjecting the black grease first to gradual heating under regulated hydrogen pressure to a temperature of around 360° F. with continuous or gradual release of admixed steam and hydrogen during the esterification until the esterification is carried to approximate completion; after which the nickel catalyst can be added to the hot esterified black grease and the hydrogenation then conducted in much the usual manner and without difficulty due to water evolution and foaming during the hydrogenation.

It is accordingly an object of the present invention to provide methods of converting black grease to obtain intermediate esterified products and final esterified and hydrogenated products of improved quality.

It is a further object of the present invention to provide a treatment of black grease which is simple and inexpensive to form a more valuable esterified product therefrom, particularly suitable for use as an intermediate in further processes.

It is a still further object of the present invention to provide a new hydrogenated product derived from black grease by regulated esterification and subsequent hydrogenation which has valuable properties as a hydrogenated product and which contains substantially all of the fatty material of the black grease, in a hydrogenated condition.

The invention will be further illustrated by the following more detailed description. To obtain the black grease, the soap stock is acidulated by boiling the same with the addition of sulfuric acid to split the soap, to decompose phosphatides and glucosides, and to free the oil. The fatty acids, oil, and unsaponifiables and coloring matter, including esterifiable constituents, enter the fatty layer on top of the acid water, which settles. The fatty material is separated from the acid water, washed, settled, and decanted. The phosphatides have the general formula, which will be hereby represented by lecithin:



Other members of the phosphatide group differ only in the nature of the group attached to the phosphoric acid. During the acidulation step these phosphatides are largely decomposed, yielding diglycerides, phosphoric acid, and in the case of lecithin, choline. The diglycerides enter the black grease and constitute a very appreciable part of it. There may also be present small and varying amounts of monoglycerides or even of glycerine. The black grease may also contain

some mono- and diglycerides removed from the crude oil by the alkali refining treatment and carried into the black grease on acidulation of the soap stock.

The black grease contains some free water, apparently held in a dissolved or emulsified state by reason of the presence of the diglycerides.

The present invention is based, as above pointed out, on the discovery that the presence of esterifiable constituents, such as diglycerides, is a primary cause for failure when attempting to hydrogenate black grease. At the temperature and other conditions necessary to effect hydrogenation the esterifiable constituents will undergo a very rapid esterification with part of the free fatty acids to form esters such as triglycerides and water in the form of steam; and the amount of steam produced is several-fold that required to completely fill the free head space of the hydrogenation vessel. Furthermore the rapid evolution of steam causes excessive foaming. For these reasons the head space is soon completely filled with steam and foam and hydrogenation ceases.

To overcome these difficulties and problems presented by the hydrogenation of black grease, the present invention provides for conducting an esterifying operation to produce an intermediate product having definite utility as such or as a preliminary step prior to hydrogenation, whereby the esterifiable constituents such as diglycerides are esterified with a portion of the free fatty acids and the water of reaction as well as the free water present in the black grease is removed.

This preliminary esterification treatment is advantageously carried out in the same apparatus in which the esterified product is to be subsequently hydrogenated. It is then heated gradually under controlled conditions in an atmosphere of hydrogen, advantageously under substantial pressure, to a temperature about 360° F. During this heating and esterifying treatment the water present as free water and that generated within the black grease mass by esterification reaction of its constituents is removed. The steam formed is withdrawn in admixture with hydrogen from time to time until the maximum temperature is reached. During this procedure the esterifiable constituents react with part of the fatty acids to form esters. Thus diglycerides are converted into triglycerides. This esterification reaction is continued until the conversion is substantially complete. As the esterification proceeds water is gradually released in the form of steam and admixes with the hydrogen and is purged from the apparatus continuously or from time to time. The rate of esterification and removal of water is controlled by the gradual and regulated heating of the black grease, by the hydrogen pressure, and by the regulated purging of admixed steam and hydrogen therefrom. The rate of heating and of esterification and of removal of water is such as to avoid excessive foaming which would result in loss of grease. Moderate pressures of hydrogen gas are advantageously maintained during the esterification treatment, e. g., from 10 to 80 pounds per square inch. The purging may take place continuously but preferably at intervals.

This esterification treatment results in the production of an esterified and dried black grease of improved fluidity. It is further distinguished from the original black grease by its substantial lack of emulsifying properties, in marked contrast with the black grease with its high content

of diglycerides, etc., which have marked water retaining and emulsifying properties.

When the preliminary esterification treatment is carried out in the hydrogenation apparatus it may be immediately followed by the hydrogenation treatment. The hot esterified black grease can thus be mixed with a small amount of a finely divided nickel catalyst and subjected to hydrogenation in the presence of hydrogen under pressure at much the usual temperatures and for usual periods of time to convert the esterified black grease into an esterified, dried and hydrogenated black grease product containing substantially all of the fatty constituents of the black grease. The hydrogenation is advantageously carried to completion or to approximate completion or to give a high melting product containing the fatty acids and fats largely as saturated fatty acids and saturated fats. In the hydrogenation unsaturated, fatty acids, whether free or combined are hydrogenated.

The resulting new esterified and hydrogenated product has a much higher titer than the original black grease or the esterified black grease. The titer may thus be as high as 50° to 63° C.; while the titer of soya bean black grease before hydrogenating may be as low as 25° C. and of cottonseed black grease as low as 35° C.

The hydrogenated product, like the esterified black grease before hydrogenation, will contain a materially increased amount of triglyceride oil and a materially lower amount of free fatty acids than the original black grease treated. The esterified and hydrogenated product may thus contain about 35% to 70% of hydrogenated glyceride oil and from 25% to 60% of free fatty acids, hydrogenated to the desired titer. It also contains around 2% to 8% or more of sterols and other unsaponifiables, including residues of glucosides. In determining unsaponifiables any sterol esters present are decomposed and the sterols appear in a free state in the so-called unsaponifiables. The amount of sterols so determined may represent an increased amount of sterol esters in the esterified, and esterified and hydrogenated, black grease. Accordingly, in referring to the content of sterols in the final product this is not limited to free sterols but includes sterol esters present in the black grease but decomposed and included in the unsaponifiable matter by the test commonly used for determining unsaponifiables.

The esterified and hydrogenated product not only contains substantially all of the fatty material originally present in the black grease, but contains the fatty materials in an improved state so that this material is a valuable product or can readily be converted into valuable products by further refining treatment. During the hydrogenation treatment not only are the unsaturated fatty acids and esters subjected to hydrogenation but other unsaturated constituents present in the black grease are simultaneously subjected to hydrogenation. While it is difficult to determine just what changes are thus brought about in impurities such as coloring matter and aromatic compounds, it seems probable that such constituents are converted to a greater or less extent into saturated or hydrogenated products. This is indicated, in the case of the coloring matter, by the lighter color of the hydrogenated product, the change of color from black to brownish, and the greater facility with which the coloring matter can be removed therefrom.

The esterified and hydrogenated product, after

decolorizing treatment, is a light colored product. It is made up principally of hydrogenated fatty acids and hydrogenated glyceride oil, with smaller amounts of other esters and unsaponifiable material, including sterols. It can be treated with agents to split the oils and set free the fatty acids, thus producing a material made up of free fatty acids and which may amount to 90% or more of the total hydrogenated product. Such hydrogenated products are useful for various purposes including use as promoters in the polymerization of unsaturated compounds in the production of synthetic rubber, and for making metallic soaps such as of aluminum, lithium, calcium and others for use as greases and the like. The fatty acid material is also useful in place of the stearic acid of commerce for various purposes.

The following are specific examples of the operation of the present invention.

Example 1

15,000 pounds of black grease or acidulated soap stock derived from soya bean oil as set forth above containing about 61% free fatty acids and other constituents including dissolved water is placed in a large closed pressure vessel. Hydrogen is introduced initially and from time to time to build up and maintain a pressure of about 10 lbs. per square inch and the vessel is gradually heated to raise the temperature from room temperature to about 360° F. over a period of about two hours. Esterification takes place with a marked reduction in the free fatty acid content of the black grease, which now becomes more fluid and oily. Due to the high temperatures the water of reaction and the free water become steam which exerts its partial pressure, and from time to time a blow-off valve is opened to release the steam admixed with hydrogen. A temperature of 360° F. is maintained and blowing off of steam and hydrogen is continued until the reactions are completed and the black grease is esterified and dried. This requires about two hours.

The esterified and dried black grease thus formed has greater fluidity than the starting material. It does not emulsify or foam as does the starting material. It is highly suitable for hydrogenation, while the starting material is difficult or impossible to hydrogenate. This product is also useful for other purposes than hydrogenation. It is, however, advantageously subjected, immediately after production and while still at a high temperature, to hydrogenation.

The catalyst for the hydrogenation is introduced into the hot esterified grease. The catalyst used may consist of a mixture of glyceride oil having about 25% of finely divided catalyst therein made up of diatomaceous earth carrying the finely divided nickel catalyst, the amount of nickel catalyst being about 10% of the glyceride oil. This catalyst is a solid black mass, granular or flakey in nature. The amount of catalyst used is about 0.3% of nickel based on the esterified black grease.

After addition of the catalyst, the pressure vessel is further heated and agitation is conducted throughout the operation. A temperature of 340° to 425° is maintained at a hydrogen pressure of about 50 to 100 lbs. per square inch. The operation is continued until the desired amount of hydrogenation has taken place and often the material is completely hydrogenated. In this stage some further esterification takes place of constituents which have not been completely esterified prior to hydrogenation or of esterifiable constituents formed during the hydrogenation. However, since only a small amount of esterification takes place, the amount of water produced thereby is small and it does not at all interfere with the hydrogenation. The hydrogenated black grease is then removed from the pressure vessel, is filtered to remove the catalyst and refined as usual, including ordinarily a bleaching operation.

Example 2

A soya black grease having 48.3% free fatty acids and diglycerides, etc., sterols, water and miscellaneous substances is treated in two stages by the procedure outlined in Example 1. The first stage of esterification and drying resulted in a material having 35.8% free fatty acids, the reduction of 12.5% being due to the esterification.

After the addition of the nickel catalyst and before hydrogenation the free fatty acids dropped to 34.4% because of the additional glyceride oil introduced with the catalyst. After the completion of the hydrogenation the free fatty acids dropped to 33.2%, the decrease of 1.2% being the result of the residual esterification. About 90% of the esterification took place in the first stage, with further esterification during the hydrogenation of constituents which had not been completely esterified prior to hydrogenation or of constituents formed during the hydrogenation.

Example 3

Black grease obtained from the refining of cottonseed oil is placed in a suitable pressure vessel. An atmosphere of hydrogen is provided. The vessel is heated to gradually raise the temperature thereof to about 350° F. As esterification takes place steam is formed and the pressure thereof is gradually built up to the desired point. A pressure of about 50 lbs. per square inch is maintained in the vessel, caused by the presence of steam and hydrogen. A blow-off valve is opened so as to bleed off a mixture of steam and hydrogen continuously, while maintaining 50 lbs. pressure in the vessel. During the operation, vented hydrogen is replaced by fresh hydrogen.

To the esterified and dried black grease there is added 0.7% of a nickel catalyst made up of a mixture of 0.2% of fresh unused catalyst and 0.5% of spent catalyst obtained from catalytic hydrogenation of refined cottonseed oil. The black grease used has a free fatty acid content of 65%. The temperature of the reaction vessel is raised to about 400° F. Agitation is continued and a pressure of about 50 lbs. per square inch is maintained until the desired degree of hydrogenation has been obtained and esterification of the remaining diglycerides and the like completed.

At the end of the procedure, the material is filtered in a suitable press. While the free fatty acid content originally was 65%, after the esterification it has decreased to about 50%.

The product may be used without refining but usually it is refined as customary. In such refining operation, it is desirable to include a bleaching step. A lighter colored product is obtained if such bleaching is conducted after the hydrogenation than if conducted before the hydrogenation.

The esterified and dried black grease has greater fluidity than the starting material. It does not emulsify or foam. It is highly suitable for hydrogenation but it is also useful without hydrogenation. For example, the triglycerides present may be separated by liquid-liquid extrac-

tion, giving an oil and a fatty acid fraction; or it may be otherwise treated.

The catalyst used in the operation is usually powdered nickel in a carrier of oil. It is intimately associated with a considerably larger amount of earthy matter such as diatomaceous earth in major amount. The catalyst may be a fresh material or may be one which has been used in hydrogenation to the extent that it has lost its selectiveness. In the latter case larger quantities are used.

The esterified and hydrogenated product made in accordance with the present invention has superior color and hardness. The split product when mixed with tall oil for soap making gives a smooth, homogeneous mass compared to a mushy, heterogeneous mass which is obtained when hydrogenated oils, such as fish oil, are mixed with the tall oil, and a superior soap results, due likely to the presence of the other substances in the product.

As a result of the hydrogenation, the fat has become stabilized. This is seen from the fact that after bleaching the product, it does not become colored on standing. New properties are imparted to the product by the various substances other than the fatty acids present therein, which render the same suitable for new industrial uses such as a catalyst in making synthetic rubber. The product is capable of being converted by refining into an edible material; the sterols and other unsaponifiable substances contained therein being assimilable, improve the nutritive value thereof. There is practically no loss of material in the procedure as distinguished from losses of 20% to 25% during the prior method of distillation of the black grease. There results a base stock, potentially high in stearic acid from a cheap raw material. The fatty acids produced by the present process command a high selling price in the market and are much cheaper to produce by the present process than by the old distillation method.

Although the invention has been described setting forth certain specific embodiments thereof, the invention is not limited to such specific examples, which are to be considered as illustrating the invention and not limiting the scope thereof. For instance, the black grease may be purified prior to the treatment. Such purification may include the removal of proteins and the like and bleaching with well-known bleaching agents, such as sodium hypochlorite, sodium perborate and persulphate, sodium chlorite or the like. However, it is preferred to conduct such a bleaching step after the hydrogenation, as a lighter colored product is obtained thereby. In place of such purification or in conjunction therewith, the black grease and/or the hydrogenated product may be subjected to adsorbent treatment with materials like fuller's earth, carbon, and similar bleaching earths and filter aids, and the product may be treated with phosphoric and citric acids and the like.

Spent catalyst from hydrogenation of purified oil may be used in the process and also waste hydrogen vented from the usual hydrogenation apparatus may be used. The catalyst may be regenerated for re-use or the catalyst may be re-used with the addition of a fresher catalyst.

The black grease may be derived from soap stock from other oils than soya bean and cottonseed, and such oils may be of animal or vegetable nature, such as fish oils, drying oils, non-drying oils, and the like. The hydrogenated product may be further esterified with glycerine or with other polyhydric alcohol to neutralize the free fatty acids to produce compositions suitable for edible or industrial uses. The conditions of the operation may be varied within wide limits. For instance, the amount of catalyst may vary considerably and the temperatures and pressures used may be higher or lower than those set forth in the specific examples. Pressures as high as 500 to 1,000 lbs. per sq. in. and temperatures substantially above 500° F. may be used.

The esterification of the black grease may take place in the presence of other gases than hydrogen, such as nitrogen, carbon dioxide and others. A vacuum may be used during the operation, particularly where the esterification is carried out in a separate apparatus from that used for the hydrogenation; and an esterification catalyst can be used. It is preferable that the rate of esterification be controlled so that water is released gradually over a period of time.

The amount of decrease of the free fatty acids during the operation may vary to a substantial degree depending on various factors, such as amount of phosphatides in the starting materials, the amount of monoglycerides and diglycerides extracted from the crude oils by the refining treatment, and the time and temperatures of treatment, character of catalyst, and others. In Example 3 the decrease was 15%. In other runs the decrease ranged from 6.7% to 15.2% with an average of 10.9%. However, the invention is not limited to these amounts as in other cases a greater or lesser decrease may be obtained. The hydrogenated product usually contains 25% to 65% free fatty acids, 2% to 8% sterols, including free and esterified sterols, and 35% to 70% glyceride oil.

It is probable that at least part of the sterols esterify under the conditions with some of the fatty acids to form esters of considerably lowered melting point, thus increasing the fluidity of the esterified black grease. In the subsequent hydrogenation it is likely that phenolic or other chromophore substances are saturated and, as a result, lose the power to develop color, so that the hydrogenated product is of lighter color.

The drying of the acidulated black grease may take place prior to the esterification, but usually this is not desirable or essential, and as the process is preferably operated, both take place simultaneously. The time required for this phase of the operation will vary with various factors, such as the amount of diglycerides and other esterifiable constituents present. In the subsequent hydrogenation the unsaturated fatty acids are hydrogenated whether in the free or the combined state in the form of glycerides.

These and other changes in the details of the operation of the invention may be made within the spirit thereof and the invention is, therefore, to be broadly construed and not to be limited except by the character of the claims appended hereto.

I claim:

1. In a method of treating black grease, the improvement which comprises placing said black grease in a vessel, heating the same to cause esterification of diglycerides and the like, removing water therefrom, adding a nickel catalyst and thereafter subjecting the same to the action of hydrogen at a sufficiently high temperature to effect hydrogenation.

2. In a method of treating black grease, the

improvement which comprises placing said black grease in a vessel, heating the same above the boiling point of water in the presence of hydrogen under pressure to cause esterification of diglycerides and the like, and venting from said vessel the steam generated thereby, adding a nickel catalyst and thereafter subjecting the same to the action of hydrogen at a sufficiently high temperature to effect hydrogenation.

3. In a method of treating black grease, the improvement which comprises placing said black grease in a vessel, heating the same gradually with venting of steam to cause esterification of diglycerides and the like, adding a nickel catalyst and thereafter subjecting the same to the action of hydrogen at a sufficiently high temperature to effect hydrogenation.

4. In a method of treating black grease, the improvement which comprises placing said black grease in a vessel, gradually heating to about 360° F. with venting of steam generated thereby during said heating to cause esterification of diglycerides and the like, adding a nickel catalyst and thereafter subjecting the same to the action of hydrogen at a sufficiently high temperature to effect hydrogenation.

5. In a method of treating black grease, the improvement which comprises placing said black grease in a vessel, heating the same to cause esterification of diglycerides and the like and simultaneously removing substantially all the water therefrom, adding a nickel catalyst and thereafter subjecting the same to the action of hydrogen at a sufficiently high temperature to effect hydrogenation.

6. In a method of treating black grease, the improvement which comprises placing said black grease in a vessel, heating the same to cause esterification of diglycerides and the like, removing water therefrom, adding a nickel catalyst, thereafter subjecting the same to the action of hydrogen at a sufficiently high temperature to effect hydrogenation, and then bleaching said product.

7. In a method of treating black grease, the improvement which comprises placing said black grease in a vessel, heating the same to a sufficiently high temperature to cause esterification of diglycerides and the like by fatty acids present in said black grease, and removing water therefrom.

8. In a method of treating black grease, the step of substantially completely drying the same at esterifying temperatures above the boiling point of water.

9. The method of treating black grease which comprises heating the same to effect esterification and drying prior to hydrogenation and then subjecting the esterified and dried grease to hydrogenation.

10. The method of producing hydrogenated black grease which comprises subjecting black grease to an esterifying and drying treatment prior to hydrogenation by gradually heating the black grease in the hydrogenation vessel under hydrogen pressure, drawing off hydrogen and steam during the esterification, continuing the esterifying and drying treatment until the esterifiable constituents of the black grease have been largely esterified to form a product which is non-foaming on further heating, adding a nickel catalyst to the hot esterified grease and subjecting the same to the action of hydrogen under a hydrogenation temperature and pressure to hydrogenate the same.

11. The method of treating black grease to increase the fluidity and reduce the free fatty acid content thereof which comprises heating the black grease to a sufficiently high temperature to effect reaction of esterifiable constituents thereof with part of the fatty acids, removing water present in the black grease and water formed by the esterification, and continuing the heating and esterification treatment until the esterified product is practically non-emulsifiable and non-foaming on further heating.

12. An esterified and dried black grease obtained by heating black grease to a sufficiently high temperature to cause esterification of diglycerides and the like by fatty acids present in said black grease.

13. An esterified, dried and hydrogenated black grease obtained by heating black grease to a sufficiently high temperature to cause esterification of diglycerides and the like by fatty acids present in said black grease and thereafter subjecting the product to hydrogenation in the presence of a hydrogenation catalyst at elevated temperatures.

14. An esterified and dried black grease obtained by heating black grease to a sufficiently high temperature to cause esterification of diglycerides and the like by fatty acids present in said black grease, said product having been bleached.

15. An esterified, dried and hydrogenated black grease obtained by heating black grease to a sufficiently high temperature to cause esterification of diglycerides and the like by fatty acids present in said black grease and thereafter subjecting the product to hydrogenation in the presence of a hydrogenation catalyst at elevated temperatures, being principally fatty acids and oil, and containing a substantial amount of unsaponifiables.

16. An esterified, dried and hydrogenated black grease obtained by heating black grease to a sufficiently high temperature to cause esterification of diglycerides and the like by fatty acids present in said black grease and thereafter subjecting the product to hydrogenation in the presence of a hydrogenation catalyst at elevated temperatures, being principally fatty acids and oil, and containing a substantial amount of unsaponifiables, in the proportions of 25%–65% fatty acids, 35%–70% oil and 2% to 8% of unsaponifiables.

17. An esterified, dried and hydrogenated black grease obtained by heating black grease to a sufficiently high temperature to cause esterification of diglycerides and the like by fatty acids present in said black grease and thereafter subjecting the product to hydrogenation in the presence of a hydrogenation catalyst at elevated temperatures, being principally fatty acids and oil, and containing a substantial amount of unsaponifiables in the proportions of 25%–65% fatty acids, 35%–70% oil and 2% to 8% of unsaponifiables, said product having a titre of 50°–63° C.

18. An improved black grease product of materially reduced free fatty acid content, the esterifiable constituents of the black grease being combined with part of the fatty acids in the form of esters, said product being free from the emulsifying properties of black grease, non-foaming on heating, and capable of being hydrogenated by usual hydrogenation treatment.

19. An esterified and dried black grease obtained by heating black grease to a sufficiently high temperature to cause esterification of diglycerides and the like by fatty acids present in said black grease, substantially free from esterifiable glycerine radicals.

20. An esterified and dried black grease obtained by heating black grease to a sufficiently high temperature to cause esterification of diglycerides and the like by fatty acids present in said black grease and containing a substantial amount of unsaponifiables.

21. An esterified and dried black grease obtained by heating black grease to a sufficiently high temperature to cause esterification of diglycerides and the like by fatty acids present in said black grease and containing 2% to 8% of unsaponifiables.

JOSEPH H. KIRBY.

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